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CARBON NANOTUBES: A RELIABLE ADDITIVE FOR THE NATURAL FIBER-REINFORCED COMPOSITES

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Abstract

Natural fiber-reinforced composites (NFRCs) has been proven to be the best alternative for synthetic fibers considering cost and environmental impacts. However, the main concerns faced by NFRCs are that they don't show satisfactory mechanical properties, exhibit poor acoustic absorption notably in lower frequency spectrums, sensitive to microbial attack and offer poor resistance to heat and flame. In order to address the above concerns, Carbon Nanotubes (CNTs) can be an effective solution that can be added as an additive to NFRCs. The trend of adding CNTs to the NFRCs has been initiated earlier. However, this process has not been explored for many applications. This review covers the effect of CNTs on the mechanical properties of the NFRCs. Addition of CNTs to the composite exceptionally increases the mechanical properties of them due to their stronger interfacial bonding, catalytic reactions, and well dispersion. A decrease in mechanical properties was mainly due to the agglomeration of CNTs in the composite. This review also explains the other advantages of CNTs in different composites. In an overall basis, this review recommends, CNTs as a reliable additive for enhancing the various properties of the NFRCs.

Keywords: Carbon nanotubes, Hybrid composites, Mechanical properties, Natural fibre-reinforced composites.

1. Introduction

Hybrid composites are those that contain more than two reinforcements in it. The usage of natural fibers as reinforcements in the composite makes them light-weighted, economic and biodegradable with balanced strength. These hybrid composites are used widely in all fields of science and engineering [1]. Figure 1 shows the evolution of composites.

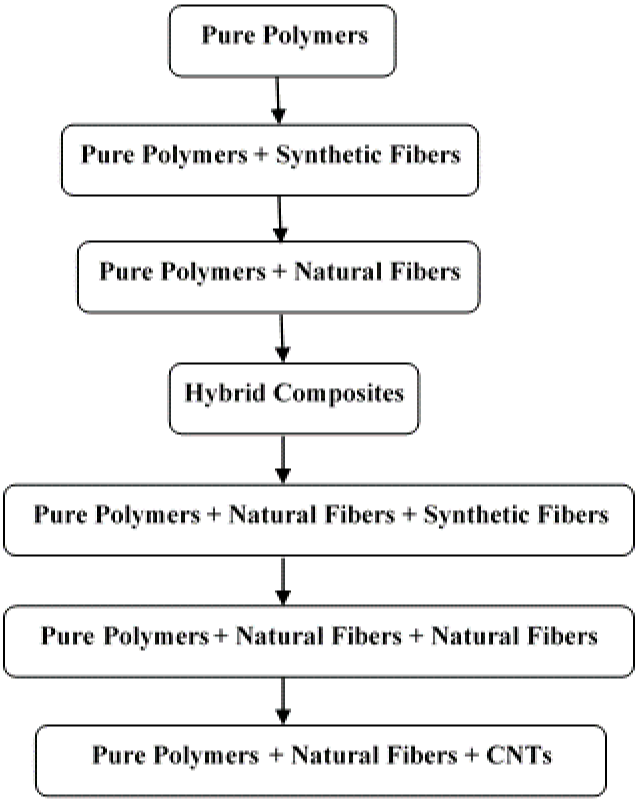

Fig. 1. Evolution of composites.

It can be noticed from Fig. 1 that polymers started the hierarchy replacing the metal components. Polymer components are light weighted, corrosive resistance and better insulators. Synthetic fibers are reinforced with polymers to produce composites with high performance in terms of strength and stiffness [2]. Considering satisfied processing cost with negligible environmental impacts at lower densities, reinforcement with natural fibers comes into play. Biodegradability, renewability and sustainability are also some of the salient features which support NFRCs [3]. NFRCs don’t exhibit satisfactory strengths compared to synthetic fiber reinforced composites thereby, paving way for hybrid composites. Synthetic fibers and natural fibers were used as second reinforcement along with NFRCs composites [4].

Some of the NFRCs-synthetic fibers and NFRCs-natural fibers are tabulated in Tables 1 and 2.

Table 1. Polymer-natural fiber-synthetic fiber [4].

Matrix	Reinforcement 1 (Natural Fiber)	Reinforcement 2 (Synthetic Fiber)	Properties Tested*
Epoxy	Bamboo	Glass	F-C
Polyester, vinyl ester	Bamboo	Glass	F-S
Polyester	Bamboo	Glass	T-C.R
Polypropylene	Bamboo	Glass	M-TH
Polypropylene	Bamboo	Glass	T-F-FA
Polypropylene	Banana	Glass	M-TH
Polyester	Banana	Glass	T-I
Polystyrene	Banana	Glass	T-F
Polyester	Curaua	Glass	M-TH
Polyester	Curaua	Glass	T-F
Epoxy	Flax	Glass	I
Phenolic	Flax	Glass	T,S,TO
Polypropylene	Flax	Glass	M
Polyester	Hemp	Glass	I-FA
Polypropylene	Hemp	Glass	T-F-I
Epoxy and phenolic	Jute	Carbon	T-F-E
Polyester	Jute	Glass	T-F
Polyester	Jute	Glass	T-F-S
Polyester	Jute	Glass	T-F-S
Polyester	Jute	Glass	F-C
Polyester	Kapok	Glass	T-H-F-CO-S
Epoxy	Kenaf	Glass	T-F-I
Polyester	Kenaf	Glass	T-F-I
Epoxy	Oil palm EFB	Glass	T-I
Phenol formaldehyde	Oil palm EFB	Glass	T-F
Polyester, vinyl ester	Oil palm EFB	Glass	T-F
Polyester	Palf	Glass	T.P
Polyester	Palf	Glass	T-F-I
Rooflite	Palmyra	Glass	T-F-I-S
Epoxy	Silk	Glass	M
Phenolic	Sisal	Aramid	T-CO
Polyester	Sisal	Carbon	T-F-C.R
Epoxy	Sisal	Glass	H-I
Polyester	Sisal	Glass	T-I-CO-C.R
Polyester	Sisal	Glass	-
Polyester	Sisal	Glass	T-F-I
Polyethylene	Sisal	Glass	T-TH
Polypropylene	Sisal	Glass	T-F-I
Poly(vinyl chloride)	Wood flour	Glass	F-I
PE,PP	Wood flour	Glass	F-H
Polypropylene	Wood flour	Glass	T

*T- Tensile, F- Flexural, I- Impact, C.R- Chemical Resistance, M- Mechanical, TH- Thermal, FA- Fatigue, TO- Toughness, E- Electrical, CO- Compressive, S- Shear Strength, H- Hardness, T.P- Thermophysical.

Table 2. Polymer-natural fiber-natural fiber [4].

Matrix	Reinforcement 1 (Natural Fiber)	Reinforcement 2 (Natural Fiber)	Properties Tested*
Epoxy	Banana	Flax	M-TH
Epoxy	Banana	Jute	T-F-I
Epoxy	Banana	Sisal	M
Polyester	Banana	Kenaf	T-F-I
Polyester	Banana	Sisal	T-F-I-T.P
Polyester	Banana	Coconut sheath	T-F
Polyester	Coir	Silk	T-F-CO
Aeso	Flax	Lyocell	F-I
Polypropylene	Kenaf	Wood flour	T
Polypropylene	Kenaf	Wood flour	T-F
Epoxy	OPEFBF	Jute	T-F-I
Polyester	Ramie	Cotton	T
Polyester	Sisal	Jute	T-F-I
Polyester	Sisal	Roselle	T-F-I
Polyester	Sisal	Silk	T-F-CO
Polyester	Sisal	Silk	C.R

*T- Tensile, F- Flexural, I- Impact, C.R- Chemical Resistance, M- Mechanical, TH- Thermal, CO- Compressive, T.P- Thermo physical.

The mechanical strengths exhibited by Polymer-Natural fiber-Natural fiber composites are not remarkable. Other factors like resistance to microbial attack, resistance to heat and flame and acoustic absorption in lower frequency spectrums also remain as concerns. Considering the above concerns, CNTs can be used as an additive to make the composites more effective in terms of all factors like strength [5], acoustic absorption [6], resisting heat, flame [7] and preventing microbial attacks [8].

2. Materials

This review focuses on the effect of adding CNTs to the NFRCs.

2.1. Carbon nanotubes (CNTs)

Carbon Nanotubes, also known as tubular fullerenes, are carbon molecules in a cylindrical shape having a diameter ranging in the order of few nanometres. They are synthesised by following techniques, arc-discharge, laser ablation, chemical vapour deposition, vapour phase growth and by flame synthesis [9]. CNTs are one of the most reliable additives with its outstanding chemical stability, thermal and electrical conductivities, and mechanical properties. They are mainly classified into two types, they are Single Walled Carbon Nanotubes (SWCNTs) and Multi Walled Carbon Nanotubes (MWCNTs) [10]. They also have exceptional strength, stiffness, aspect ratio and flexibility with low weight. These CNTs have been widely used in applications of biomedical, sensors and electronic devices [11].

2.2. Effect of different types of CNTs on mechanical properties

Gojny et al., studied the effect of different types of CNTs which are single, double and multi walled on mechanical proeprties of the composite. Epoxy was used as matrix in the composite. Recently, double, triple and other walled of CNTs except single walled structure are grouped under MWCNTs. They found that addition of CNTs increased the mechanical properties of the composite. It was applicapble for all the types of CNTs with addition of initial contents whereas, further addition of CNTs decreases the mechanical properties of the system in case of double walled and multi walled CNTs. Tensile strength of the composite with addition of 0.05, 0.1 and 0.3 wt% SWCNTs was found to be 65.54 MPa, 66.34 Mpa and 67.28 MPa respectively whereas, tensile strength of the composite with addition of 0.1, 0.3 and 0.5 wt% double walled and multiwalled CNTs were 62.43 MPa, 67.77 MPa, 67.66 MPa and 62.97 MPa, 63.17 MPa, 61.52 MPa respectively. Thay have concluded the followings aspects; In general, increase in mechanical properties of the composite is attributed by transfer of stress occurring via the outermost layers of CNTs. Mechanical reinforcement of SWCNTs remains as concern considering the above factor. It is therefore evident that MWCNTs with more outer walls offers much interface and resistance to external force thereby increasing the mechanical properties of the composite. However, larger the interface, the more concern on dispersion CNTs in the matrix. SWCNTs easily disperse in matrix and the chances of agglomeration are less compared to MWCNTs. Hence CNTs exhibiting lesser specific surface area with optimized dispersion could be the solution for enhacement in mechanical properties of the composite [12].

2.3. Modification of CNTs

Napisah et al. inspected the effect of acid and silane treatment on MWCNTs for the mechanical properties of the NFRCs. The effect of Pristine (Original) CNTs (PCNTs) was compared with Acid treated CNTs (ACNTs) and Silane treated CNTs (SCNTs). Acid treatment was made by dispersing CNTs in 300 ml of sulphuric and nitric acid with a ratio of 3:1 at 80 ℃ for 4 hours, followed by adding distilled water to the solution and allowing to stir for 6 hours continuously. The mixture was further filtered with distilled water and acetone till pH value reached 6 to 7. Finally, the oxidized CNTs were dried for 24 hours at 80 ℃. For the silane treatment, the obtained oxidized CNTs were dispersed in 2% 3-Aminopropyltriethoxysilane, which was diluted in 300 ml ethanol-water (95:5, v/v). The mixture was stirred at 70 ℃ for 4 hours and finally filtered with distilled water and acetone. It can be noted that modifying the CNTs with silane increases the tensile strength by 43.30%, flexural strength by 21.10% and impact strength by 130%. Silane modification reduces the agglomeration of CNTs in the matrix and provides better dispersion which in turn exhibits better results than PCNTs and ACNTs [13].

2.4. Natural fibre-reinforced composites (NFRCs)

There are wide number of polymers available which varies based on occurrence, mode of formation, physical properties, line structure and thermal response which can be reinforced with different varieties of natural fibers like, Bast (flax, kenaf, roselle, hemp, ramie, mesta, jute), Wood (soft, hard wood), Fruit (coir, oil palm), Seed (cotton, kapok, milk weed, loofah), Stalk (wheat, rice, barley, rye, oat, maize), Leaf (banana, sisal, henequen, abaca, raphia, pineapple, agave) and Grass (bamboo, bagasse, rape, esparto, corn, sabai, canary) [14].

3. Methods

CNTs are dispersed in polymers mainly by three methods namely, melt blending, solution mixing and in situ polymerisation [15]. Ball milling which is known as mechanical milling is receiving attention in recent years. This is because, it overcomes some of the concerns of the melt blending process where, the composites will be exposed to enormous heating and in case of solution mixing, it is a tedious process to get rid of solvent phase after dispersion [16]. Table 3 shows some of the literature made on NFRCs-CNTs hybrid composites.

Table 3. Literatures Based on NFRCs-CNTs Hybrid Composites and its Constituents.

Matrix	Natural fiber /Filler	CNTs Content (%)	Type of CNTs	Method of Dispersion	Composite Preparation Technique	Properties Discussed*	Ref. No.
Polypropylene	Poplar Wood	0-3.5	MWCNTs	Melt Blending	Injection Molding	T-F-I	[17]
Polypropylene	Sugarcane	0-3.5	MWCNTs	Melt Blending	Injection Molding	T-F-I	[17]
Epoxy	Ramie	0.4	MWCNTs	Solution Mixing	Compression Molding	C	[18]
Epoxy	Ramie	0-0.6	MWCNTs	Solution Mixing	Hand Layup & Compression Molding	S-F	[19]
Epoxy	Kenaf	0-1	PCNTs/ACNTs /SCNTs	Solution Mixing	Filament Winding & Hand Layup	T-F-I	[13]
Epoxy	Bamboo	0.15	CNTs	Solution Mixing	Hand Layup & Compression Molding	T-F-I	[20]
Epoxy	Bamboo	0-3	CNTs	Solution Mixing	Hand Layup & Compression Molding	T-F-I	[21]
Epoxy	Jute, Banana& Flax	0-1	MWCNTs	Solution Mixing	Compression Molding	T-C-I-H	[22]
Epoxy	Bamboo/Glass	0-1	MWCNTs	Solution Mixing	Hand Layup & Compression Molding	T-F	[23]
Epoxy	Kenaf/Glass	0-1	MWCNTs	Solution Mixing	Filament Winding & Hand Layup	T-F	[24]
Epoxy	Banana /Glass	0-1	MWCNTs	Solution Mixing	Compression Molding	T-CO-F	[25]
Epoxy	Flax /Glass	0-1	MWCNTs	Solution Mixing	Compression Molding	T-CO-F	[26]
Polyurethane	Cotton	5-8	MWCNTs	Solution Mixing	Compression Molding	T	[27]
PLA	Basalt	1	MWCNTs	Melt Blending	Injection Molding	T	[28]
PLA	Kenaf	1	MWCNTs	Melt Blending	Compression Molding	T-I	[29]

*T- Tensile, F- Flexural, I- Impact, CO- Compressive, S- Shear Strength, H- Hardness, C- Creep.

CNTs were dispersed by melt blending [17, 28, 29] and dispersed by solution mixing [13, 18-22, 27] to the NFRCs. Poly(lactic acid), polypropylene (PP), epoxy and polyurethane (PU) are some of the matrices which are reinforced with natural fibers/fillers like poplar wood, sugarcane, ramie, kenaf, bamboo, jute, banana, flax, cotton and basalt. In a few works of literature, glass was used as a constituent along with NFRCs/CNTs composite [23-26]. In the case of PLA based hybrid composites; only 1 wt% of CNTs content has been investigated [28, 29]. In the PP based hybrid composites; the percentage of weight content of CNTs was investigated up to 3.5 wt% [17]. In the case of PU based hybrid composites, 5 wt% to 8 wt% of CNTs content were investigated [27] whereas, in the epoxy-based hybrid composites, CNTs content up to 3 wt% has been analysed [13, 18-26].

Compression molding, injection molding, hand Layup and filament winding are the techniques used for preparing these hybrid composites.

4. Mechanical Properties

Tensile, flexural, impact, compression, creep, shear and hardness of the hybrid composites are considered as factors for investigating the effect of CNTs on mechanical properties of different NFRCs.

4.1. Tensile properties

It can be seen from Table 3 that the majority of the researches have been involved in evaluating the tensile properties of the hybrid composite [13, 17, 20-29]. The tensile strength of the hybrid composites was ranging from 10 MPa to 70 MPa. Tensile strength of the composites which are produced by dispersing CNTs through melt blending ranges from 48 MPa to 70 MPa [17, 28, 29] whereas, a tensile strength of the composite which are produced by dispersing CNTs through solution mixing ranges from 10 MPa to 45 MPa [13, 20-22, 27]. Interestingly, few papers discussed the mechanical properties of the hybrid composite with glass fibers as a constituent in it along with natural fibers, matrix and CNTs. In those hybrid composites, the tensile strength was ranging from 45 MPa to 433 MPa [23-26]. The trend of the effect of CNTs content on the tensile properties of the NFRC can be seen in the below Figs. 2 and 3.

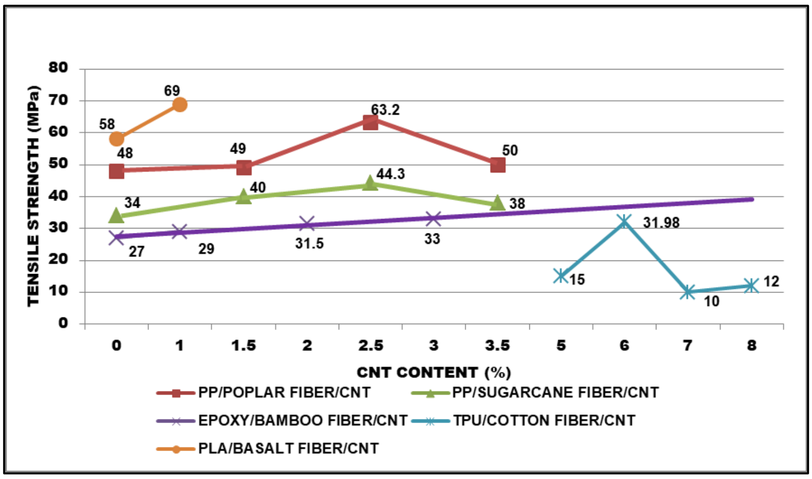

Fig. 2. Effect of CNTs content on tensile strength of NFRCs

From Fig. 2, it can be noticed that the tensile properties of the composites

(i) Increases suddenly from 49 MPa to 63.2 MPa for 1.5% & 2.5% CNTs and decreases to 50 MPa for 3.5% CNTs for PP/Poplar fiber/CNTs

(ii) Decreases from 44.3 MPa to 38 MPa for 2.5% & 3.5% CNTs for PP/sugarcane fiber/CNTs

(iii) Increases linearly for PLA/Basalt fiber/CNTs and epoxy/bamboo fiber/CNTs

(iv) Increases, decreases and once again decreases for TPU/cotton fiber/CNTs.

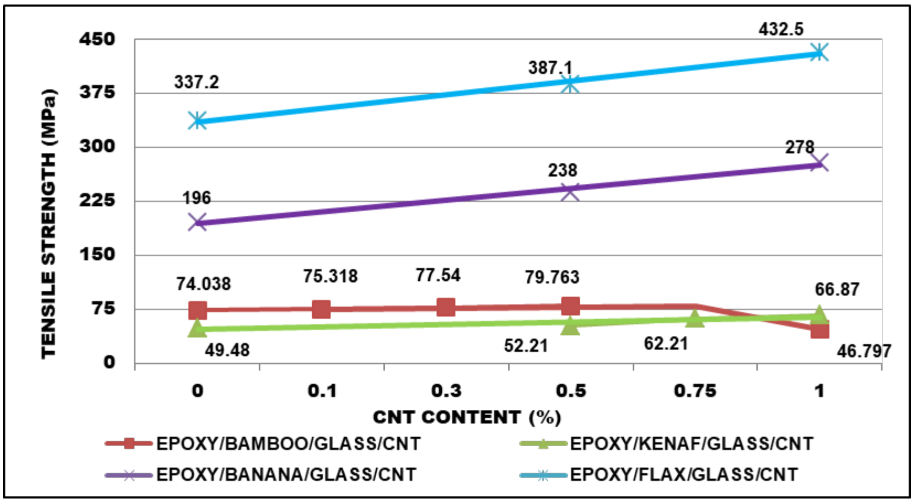

Fig. 3. Effect of CNTs content on tensile strength of glass/NFRCs.

It can be noted from Fig. 3 that, there is an increase in tensile strength of the composite with an increase in CNTs content for epoxy/banana, kenaf, flax/glass composite. Only for epoxy bamboo/glass/CNTs composite, the tensile strength is almost constant and decreases as % of CNTs increases. Along with the tensile strength, tensile modulus has also been reported in a few papers [17, 23, 24, 28]. Tensile modulus of the NFRCs/CNTs composite ranges from 2.3 GPa to 3.9 GPa and tensile modulus of the NFRCs/Glass/CNTs composite ranges from 1.8 GPa to 6.5 GPa. Tensile modulus of the composites produced by melt blending CNTs ranges from 2.8 GPa to 3.9 GPa whereas, the tensile modulus of the composite produced by solution mixing ranges from 1.8 GPa to 6.5 GPa. Trends of the effect of CNTs content on the tensile modulus of the NFRCs is shown in Fig. 4 and the effect of CNTs content on the tensile modulus of the Glass/NFRCs is shown in Fig. 5.

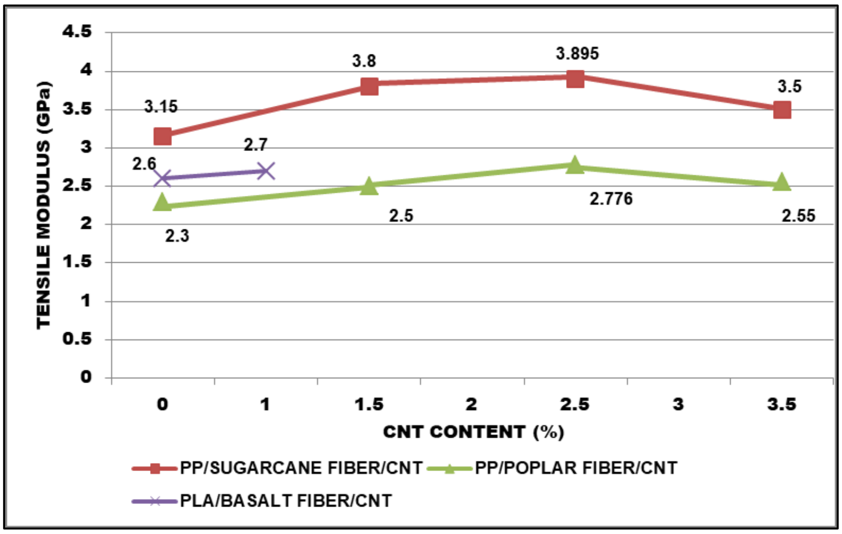

Fig. 4. Effect of CNTs content on tensile modulus of NFRCs.

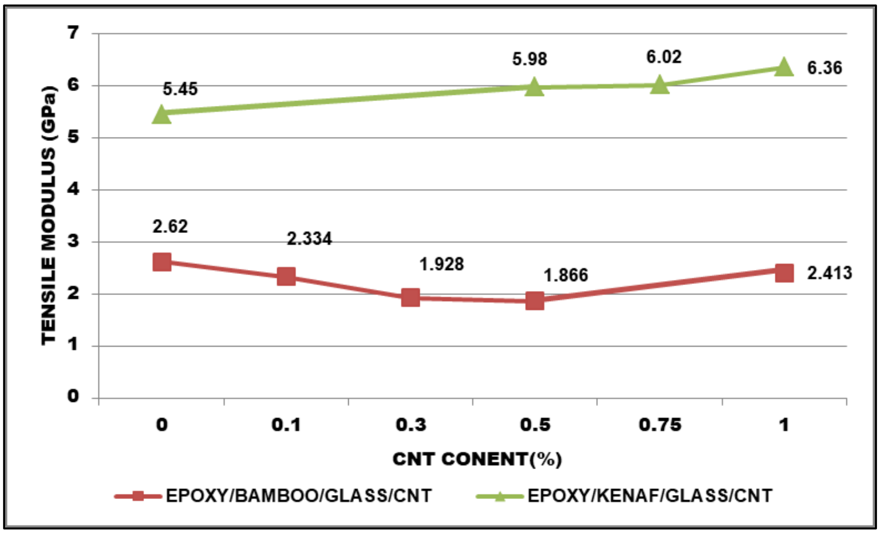

Fig. 5. Effect of CNTs content on tensile modulus of glass/NFRCs.

It can be observed from Figs. 4 and 5 that, there is an increase in tensile modulus of the composite having sugarcane, poplar, basalt, kenaf/glass with an increase in CNTs content and a further increase of CNTs content, decreases the tensile modulus of the composite having sugarcane and poplar. Only in the case of epoxy/bamboo/glass/CNTs composite, a reverse trend is seen where, increase in CNTs content decreases the tensile modulus and further increase in CNTs content, increases the tensile modulus of the composite.

4.2. Flexural properties

The effect of CNTs on the flexural properties of the NFRCs has been investigated by a few of the literature [17, 19-21, 23-26]. The flexural strength of the hybrid composites was ranging from 32 MPa to 238 MPa. The flexural strength of the composite produced by melt blending CNTs ranges from 32 MPa to 44 MPa [17] whereas, a flexural strength of the composite which are produced by dispersing CNTs through solution mixing ranges from 60 MPa to 238 MPa [19-21, 23-26]. The flexural strength of the composite with glass as one of the reinforcement ranges from 55.55 MPa to 238 MPa [23-25]. In one paper, the flexural load carrying capacity of the composite was investigated. It was found that the flexural load carrying capacity increases with an increase in the percentage of CNTs. At 1 wt % of CNTs content, the maximum flexural load-carrying capacity of 9.23 KN was achieved [26]. The trend of the effect of CNTs on the flexural properties of the NFRCs and NFRCs/Glass composites can be seen in the below Figs. 6 and 7.

It can be noticed from Figs. 6 and 7 that, the trend of the effect of CNTs content on the flexural strength of the composite is similar to the trend seen with the tensile strength. Increase in CNTs content increases the flexural strength of the composite and further increase in CNTs content leads to a decrease in flexural strength in a few cases. In particular, a flexural strength of the epoxy/ramie, bamboo and banana/glass composite increases linearly with increase in CNT content whereas, in case of PP/sugarcane, PP/poplar and epoxy/kenaf/glass composite, its tensile strength increases gradually and suddenly decreases with increase in CNT content.

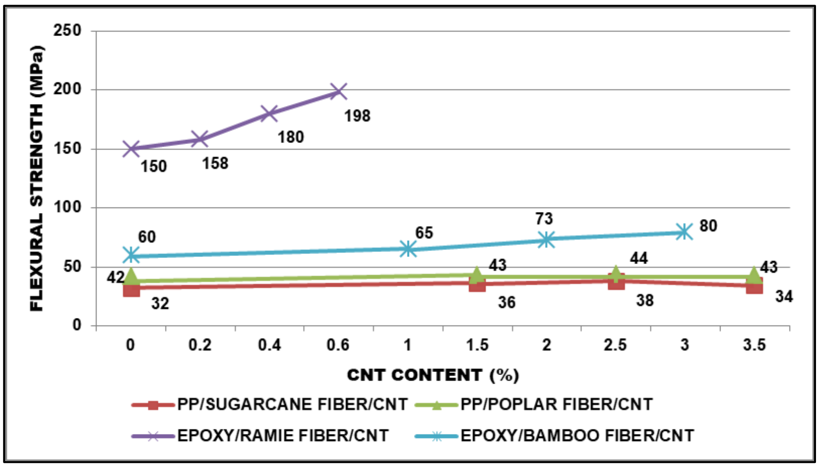

Fig. 6. Effect of CNTs content on flexural strength of NFRCs.

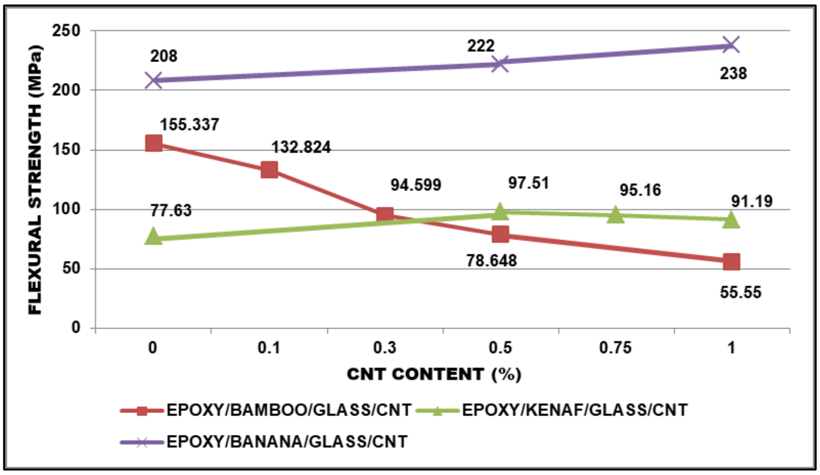

Fig. 7. Effect of CNTs content on flexural strength of glass/NFRCs.

An opposite trend was seen in the case of epoxy/bamboo/glass/CNTs where an increase in CNTs content decreases the flexural strength of the composite. Along with the flexural strength, flexural modulus has also been reported in a few papers [17, 19, 23, 24]. Flexural modulus of the composites produced by melt blending CNTs ranges from 3 GPa to 3.45 GPa [17] whereas, the tensile modulus of the composite produced by solution mixing ranges from 10 GPa to 13.5 GPa [19, 23, 24]. The trend of the effect of CNTs on the flexural modulus of the NFRCs and NFRCs/Glass composites can be seen in the below Figs. 8 and 9.

It can be noted from Figs. 8 and 9 that, there is an increase in flexural modulus of the composite with increase in CNTs content for PP/sugarcane, PP/poplar, epoxy/ramie and kenaf/glass and further increase of CNTs content, decreases the flexural modulus of the composite in PP/poplar and PP/sugarcane composites. Only in the case of Epoxy/Bamboo/Glass/CNTs composite, a reverse trend is seen where an increase in CNTs content decreases the flexural modulus of the composite.

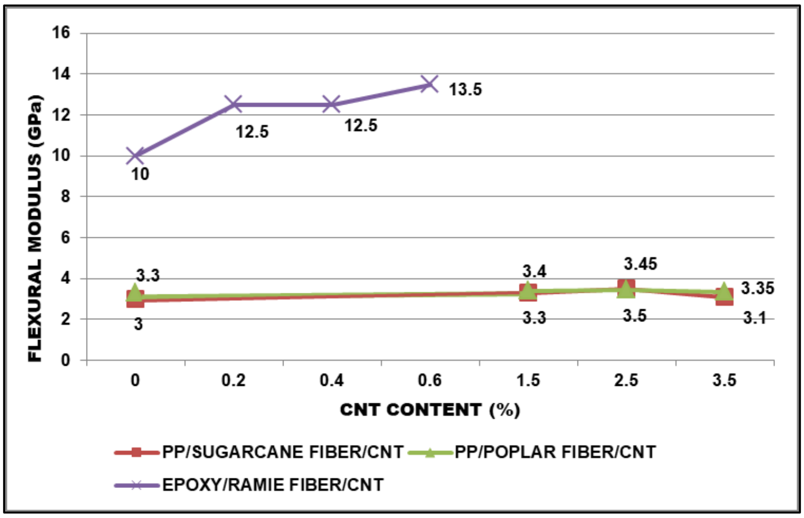

Fig. 8. Effect of CNTs content on flexural modulus of NFRCs.

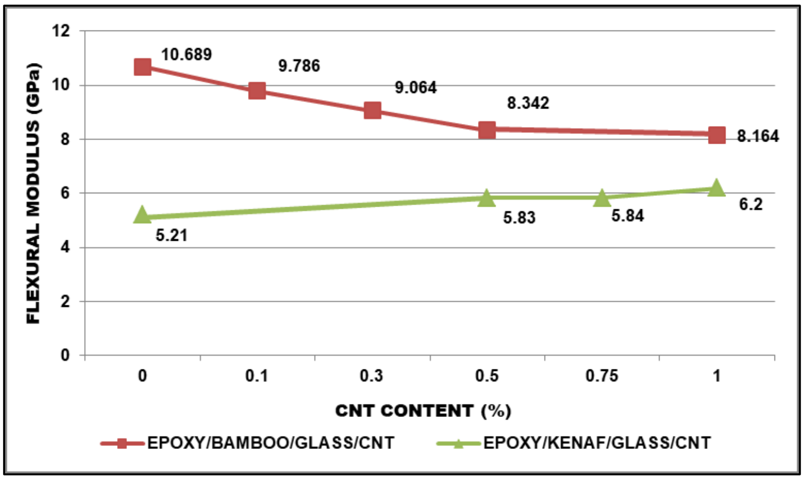

Fig. 9. Effect of CNTs content on flexural modulus of glass/NFRCs.

4.3. Impact properties

The effect of CNTs on the impact strength of the NFRCs has been investigated by a few of the literature [17, 20, 21 29]. The impact strength of the CNTs added NFRCs ranges from 22 Jm-1 to 90 Jm-1. The trend of the effect of CNTs on the impact strength of the NFRCs can be seen in Fig. 10.

It can be observed from the Fig. 10 that, there is an increase in impact strength from 30 Jm-1 to 35 Jm-1 for PP/sugarcane at 1.5 wt% of CNTs and 23 Jm-1 to 26 Jm-1 for PP/poplar composite at 2.5 wt% of CNTs and decreased to 31 Jm-1 and

22 Jm-1 at 3.5 wt% of CNTs respectively. Only in the case of bamboo reinforced composite, a reverse trend can be seen where increase in CNTs content, decreases the impact strength of the composite.

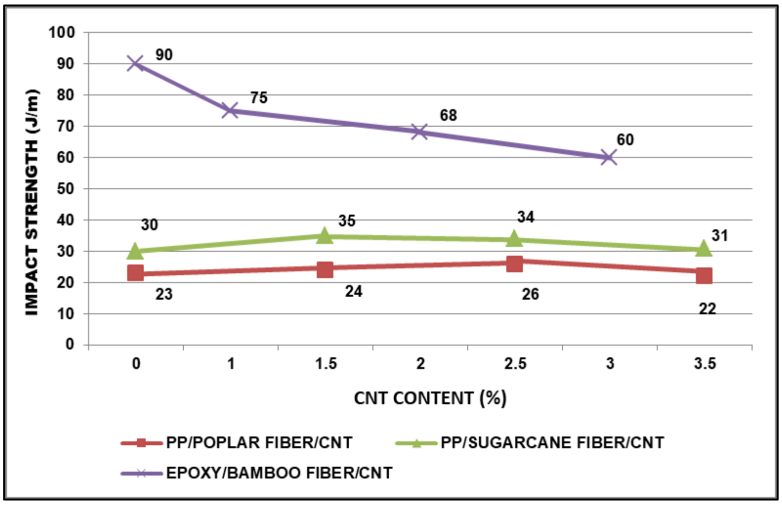

Fig. 10. Effect of CNTs content on Impact Strength of NFRCs.

In a few papers, a fixed percentage of CNTs content was investigated on the mechanical properties of the composite. Chen et al., examined the mechanical properties of the hybrid composite before and after annealing. 1 wt% of modified CNTs was added along with kenaf fibers. Once the composite is produced, annealing treatment at 80 ℃ for 8 hours was performed. It was seen that annealed composites exhibit better performance and they concluded annealing will be the reason for controlling the mechanical properties of the composite [29].

Kushwaha et al., added 0.15 wt% of CNTs content along with bamboo reinforced epoxy composite. They investigated the effect of CNTs on water absorption and mechanical properties of the composite. They found the addition of 0.15 wt% CNTs content increases the tensile strength by 6.67 %, tensile modulus by 2.7 %, flexural strength by 5.8 % and flexural modulus by 31 % respectively. Ultimately, the impact strength of the composite increases by 84.5 % and water uptake of the composite reduced to 23.18 % respectively [20].

4.4. Compressive, creep, shear and hardness

Compressive properties of the CNTs reinforced hybrid composite was investigated only in two papers [25, 26]. In both the papers, glass was one of the constituents along with NFRCs/CNTs. In case of Epoxy/Banana fiber/Glass/CNTs, it can be noted that the compressive strength increases with increase in CNTs content [25] whereas, in case of Epoxy/Flax fiber/Glass/CNTs composite, compressive properties are not enhanced on adding CNTs. Authors suspect that the formation of air voids in the composite during the testing as a reason for a decrease in compressive properties [26].

Creep of the NFRCs/CNTs hybrid composited was reported by [18]. It can be seen that the creep resistance of the composite with CNTs is higher than the composite without CNTs. It was concluded that CNTs restricts the mobility of molecular chains of the matrix and also helps in holding the matrix and the ramie fiber, thereby increasing the creep resistance of the composite [18].

Shen et al., investigated the interlaminar shear strength (ILSS) of the NFRCs with and without CNTs. It can be seen that the ILSS of the composite with CNTs increases by 38%. The authors concluded that the catalytic action of CNTs enhanced the area of reaction between the matrix and the ramie fiber, which in turn increases the ILSS of the composite [19].

Mohan and Rajmohan fabricated two types of composites using jute, banana and flax fiber were prepared. In one composite, bottom and the top layer was the jute fiber and in the other composite, flax fiber was laid as the bottom and top layer. They inspected the mechanical properties of those composite with the addition of CNTs. It was seen that there is an increase in tensile strength, compressive strength and hardness of the composites with an increase in CNTs content in case of both composites. In case of impact strength, there is an increase in impact strength with increase in CNTs content in the composites with flax fiber at bottom and top and the opposite trend was seen in the composites with jute fiber in the top and bottom layer [22].

5. Factors Influencing the Mechanical Properties of the NFRCs/CNTs Composites

In a review paper by Randjbaran et al., interlocking, pull-out, van der waals forces, agglomeration, chemical reaction and energy absorption are the factors listed, which are responsible for influencing the mechanical properties of the composite. The above-mentioned paper mainly dealt with epoxy as a matrix whereas, in this review, polymer matrices like PLA, epoxy, PU, PP are used. It can be seen that there is an increase in mechanical properties of the PP/poplar wood and sugarcane, epoxy/banana, ramie, kenaf and flax, PU/cotton, PLA/basalt with increased addition of CNTs content and a further increase of CNTs content, decreases the mechanical properties in few cases. A reverse trend was seen only for bamboo reinforced hybrid composites in some discussions. Table 4 shows the factors responsible for increase in mechanical properties of the CNTs based hybrid composites.

Table 4. Factors infulencing the mechanical properties of the CNTs based hybrid composites.

Matrix	Reinforcements and Additives	Factors for Increase/ Decrease in Mechanical Properties	References
Epoxy	Ramie, Bamboo and MWCNTs	Interfacial Bonding Strength	[19, 20]
Epoxy	Ramie and MWCNTs	Chemical, Catalytic Reactions	[18, 19]
Polypropylene	Poplar Wood, Sugarcane and MWCNTs	Dispersion	[17]
Polypropylene	Poplar Wood, Sugarcane and MWCNTs	Agglomeration	[17]

5.1. Interfacial bonding strengths

Increase in mechanical properties was mainly due to the special bonds in CNTs, which were able to hold the matrix and fibers, thereby exhibiting good interface between them [19, 20].

5.2. Chemical reaction

The chemical reaction of the carboxylic groups on MWCNTs helps in restricting the mobility of the molecular chains in the polymer matrix which shows improved creep resistance [18]. This action of constraining the movement of polymer chains also resulted in improved flexural properties, heat resistance and glass temperature but declined the impact toughness. The catalytic reaction of CNTs increased the reaction between the matrix and reinforcement resulting in enhanced shear strength [19].

5.3. Dispersion of CNTs

There are cases where CNTs are well dispersed and agglomerated during the stirring process. At 1.5 wt% and 2.5 wt% of CNTs content, the fine state of dispersion has been reported which, contributed to the better stress or strain distribution in the composites [17]. Melt blending and solution mixing are the techniques reported used for dispersing CNTs in the NFRCs based hybrid composites.

5.4. Preparation techniques

Injection molding, compression molding, hand layup and filament winding are the techniques reported for producing NFRCs based hybrid composites. It can be noted that the tensile strength of the hybrid composites produced by injection molding [17, 28] seems to be higher than the tensile strength of the composite produced by compression molding [21, 27]. Flexural strength of the composite produced by compression molding [19, 21] was higher compared to injection molding [17]. Also, composite produced by compression molding [21] exhibits higher impact strength than the composite produced by injection molding [17]. Considerable differences in the range of mechanical properties of the composites can be seen. This may be because of the method of preparing the composites to vary. However, this discussion cannot be conclusive, since only a few investigations are available in the literature. Thus, this technique of adding CNTs to the NFRCs should be explored.

5.5. Agglomeration

The decrease in mechanical properties was mainly due to the agglomeration of CNTs in the matrix. Increased content of CNTs (3.5 wt%) causes agglomeration in the composite which arrested the stress transfer within the composite [17].

6. Other Advantages and Applications of CNTs Reinforced composites

Other than the effect of CNTs on the mechanical properties of the NFRCs, only a few properties of the hybrid composites were investigated. Bonds of CNTs help in enhancing the interfacial interaction among polymer matrices like epoxy and natural fibers [18]. Also, CNTs helps in increasing the glass transition temperature of the composite and storage modulus [19].

In general, CNTs as an additive provides a wide range of advantages to the composite. CNTs exhibit excellent electrical conductivity and provide good corrosive resistance. CNTs being excellent transporter of electrons and higher affinity towards electron makes them be used in the field of photovoltaic [30].

CNTs inhibit the effect against microbial action by various mechanisms and hence are used in biomedical applications. CNTs are also used in membranes for ultra-filtration of water since it has good anti-microbial characteristic [8].

CNTs can retard flames and hence can be used for applications in which fire and heat will be involved [7]. Wu et al., produced a composite containing graphene foam and poly(dimethylsiloxane) which tends to be having better acoustic absorption. In the above composite, CNTs has added an additive which extends the acoustic absorption of the composite into a lower frequency spectrum. The acoustic absorption coefficient was found to be over 0.3 at a frequency range between 100-1000 Hz [6].

These above advantages are mainly considered as concerns for NFRCs. Only the effect of CNTs on the mechanical properties on NFRCs has been explored. Hybrid composites with CNTs as an additive to the NFRCs are not explored for the above applications. Hence need further investigations.

7. Limitations

The positive effects of CNTs have been summarized above. At the same time, CNTs also have some of the limitations. CNTs in market are costly and also the techniques to produce CNTs are expensive, CNTs are comparatively costlier than other carbon nanoparticles which are available [31], surface of the CNTs being in such a way that they are hard to be soluble in aqueous media [32], they are complicated for handling because of their sizes [33]. Toxicology of CNTs is one of the highly debated topics with lots of investigations are being made. CNTs are reported to exhibit in-vivo and in-vitro toxicities. Oxidative stress, agglomeration and physical interactions are the mechanisms by which CNTs exhibit their toxicity [34]. Therefore, it is highly recommended to use CNTs with proper care and handling.

8. Conclusions

This article reviewed the literature that covered the effect of the addition of carbon nanotubes on various properties of the NFRCs. Addition of CNTs to the composites shows a positive effect on mechanical properties. CNTs with its special interfacial bonding to hold the matrix and the fiber, catalytic or chemical reaction to restrict the movement of matrix and its good dispersion state helps in enhancing the mechanical properties of the composite. Agglomeration of CNTs cracked the stress transfer within the composite resulting in decreased mechanical properties. Along with that, few other properties and advantages of having CNTs in the composite are covered. This review highlights the importance of CNTs as an additive in the hybrid composites which in turn will lead to the discovery of novel composites for various applications. This review will help the upcoming researchers to identify similar kind of additives to make the composites, more effective.

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Abbreviations

ACNTs	Acid treated Carbon Nanotubes
CNTs	Carbon Nanotubes
MWCNTs	Multi Walled Carbon Nanotubes
NFRCs	Natural fiber-reinforced composites
PCNTs	Pristine Carbon Nanotubes
PLA	Poly(Lactic Acid)
PP	Polypropylene
PU	Polyurethane
SCNTs	Silane treated Carbon Nanotubes
SWCNTs	Single Walled Carbon Nanotubes

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